

Synthesis, Characterization, and Antimicrobial Activity of Carboxylate-Bridged Homodinuclear Schiff Base Metal(II) Complexes.

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ABSTRACT

The condensation reaction between 2-aminobenzoic acid and 3-nitrobenzaldehyde was used to synthesize the Schiff base (HL). Metal complexes of the Schiff base with Mn(II), Co(II), Ni(II), Cu(II), and Cd(II) were synthesized and characterized by physical and spectroscopic techniques. Elemental analyses indicated the ligand coordinated to the metal ions in the ratio 2:1 with distorted octahedral geometry. Infrared spectra and magnetic susceptibility measurements suggested a carboxylate bridge of metal-oxygen-carbon-oxygen-metal (M-O-C-O-M) mode linking two metal centers in each complex. The nature of magnetic interactions in the metal complexes was paramagnetic for Mn(II), Co(II), Ni(II), and Cu(II) and diamagnetic for Cd(II) at room temperature. Molar conductance measurements indicated the metal complexes are non-electrolytes in dimethylsulfoxide.

The Schiff base and the metal complexes were screened *in-vitro* for antimicrobial activity against eight bacterial and two fungal strains. The highest activity was observed with Cd(II) complex. The other compounds exhibited varying degrees of activity against these microorganisms.

(Keywords: Schiff base; carboxylate-bridged, homodinuclear metal complexes; antimicrobial).

INTRODUCTION

The design and synthesis of coordination complexes of transition metals with multifunctional bridging ligands is of great interest, due to their interesting topologies and wide potential applications (Shit *et al.*, 2009; Mautner *et al.*, 2011). Many Schiff base ligands have been known for their biological activity and findings from research have shown that -HC=N linkage plays an essential role (Prashanth *et al.*, 2013; Kumaran *et*

al., 2013; Kostova and Saso, 2013). Schiff bases are regarded as privileged ligands because they can easily be made by one-pot condensation reaction between aldehydes and amines and have shown extensive coordination abilities with different metal ions.

Metal complexes derived from Schiff bases are very important owing to their biological, industrial, medicinal and analytical applications (Kumar *et al.*, 2009, Mounika *et al.*, 2010, Prakash and Adhikari, 2011; Kostova and Sosa, 2013). The carboxylate group is one of the most widely used bridging ligands for designing polynuclear complexes having different structural features (Mautner *et al.*, 2011). The versatility of this group as a ligand is illustrated by the variety of its coordination modes when acting as a bridge (Yang *et al.*, 1999; Siddiqi *et al.*, 2014). The approach here is to synthesize metal complexes derived from a Schiff base ligand with both azomethine function and carboxylate group, capable of chelating and bridging to metal centers. In this work, a Schiff base ligand with azomethine and carboxylate functionality was prepared and its metal(II) complexes were derived. The characterization results for the metal complexes have been discussed.

EXPERIMENTAL

Materials and Methods

The materials and reagents were obtained from commercial supplier (Sigma Aldrich) and were used without further purification. CHN analysis of the metal complexes was carried out on Elemental Analysensysteme varioMICRO V1.6.2 GmbH. The percentage metal content in each complex was determined by standard EDTA complexometric titration. Melting points were determined on a Gallenkamp melting point

apparatus. The infrared spectra of the compounds were determined in the region 4000–350 cm^{-1} on Perkin Elmer spectrum 11 FT-IR Spectrophotometer. Magnetic susceptibility of each metal complex was obtained on Sherwood magnetic susceptibility balance and diamagnetic corrections were calculated from Pascal's constants. The electronic spectra were obtained on Labomed double beam UV-visible Spectrophotometer in the ranges 190–400 nm and 400–900 nm for UV and visible regions respectively. The molar conductances of the metal complexes in DMSO at 10^{-3} M were measured on 4150 Jenway conductivity meter.

Synthesis of Schiff Base

2((3-nitrobenzylidene)amino)benzoic acid Schiff base was prepared as follows: Ethanol solution containing 5.5 g (0.036 mol) of 3-nitrobenzaldehyde was added gradually with stirring to ethanol solution containing 5.0 g (0.036 mol) of anthranilic acid and the mixture was refluxed for 2 h at 60-70°C. The resulting light yellow precipitate was filtered, washed with ethanol, dried under vacuum and recrystallised from hot ethanol. The analytical data are recorded in Table 1.

Synthesis of Metal Complexes

The metal(II) complexes were prepared as follows: Ethanol solution containing appropriate mass (0.70 mmol) of each metal salt ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) was added gradually with stirring to ethanol solution containing Schiff base, HL, (1.39 mmol) and six drops of triethylamine (TEA). After the addition was complete, the mixture was refluxed for 2 h. The resulting precipitate was filtered, washed with a mixture of diethyl ether and ethanol, and dried in vacuum over silica gel. A similar procedure was used to synthesize Cd(II) complex using an aqueous solution of $\text{CdCl}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$.

IN-VITRO ANTIMICROBIAL SCREENING

The ligand and complexes were screened for *in-vitro* activity against the following strains of pathogens: *Bacillus subtilis* ATCC 6633, *Staphylococcus aureus* ATCC 6538, Methicillin-resistant *Staphylococcus aureus* (MRSA),

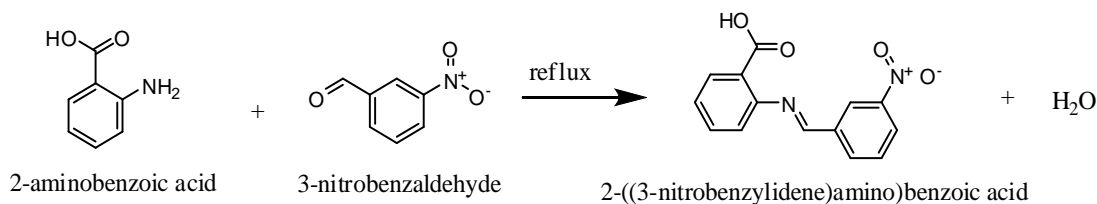
Escherichia coli ATCC 25922, *Escherichia coli* ATCC 23218, *Salmonella typhi* ATCC 33458, *Klebsiella pneumoniae* ATCC 13883, *Pseudomonas aeruginosa* ATCC 29853, *Candida albicans* ATCC 10231 and *Trichophyton rubrum* ATCC 28189. The nutrient agar and potato dextrose agar media for antibacterial and antifungal screening were prepared according to standard procedure (National Committee for Clinical Laboratory Standard. NCCLS, Villanova PA USA, 1999).

Agar-well Diffusion Technique

Agar-well diffusion technique was employed to measure the diameter of zone of inhibition of the microbial growths on plates, following standard procedure (National Committee for Clinical Laboratory Standard. NCCLS, Villanova PA USA, 1999). Wells were dug on the agar medium, using a sterile metallic cork-borer of 12 mm diameter, and inoculated with each microbial strain. Separate plates were used for each type of microorganism in order to avoid cross-contamination. 5 mg/mL of each sample was prepared in DMSO and 100 μL was delivered into the wells using a micropipette, hence 500 μg sample/well was used in the screening procedure. The plates were incubated at 37°C for 24 h and 72 h for the bacterial and fungal assays respectively. During this period, the test solution diffused and the growth of the inoculated microorganisms was affected. The inhibition zones developed on the plates were measured after 24h and 72h, respectively. The results are recorded in Table 3.

Minimum Inhibitory Concentration

The minimum inhibitory concentration (MIC) of the complexes was determined by serial dilution two-fold technique using 96-well microtitre plates. The MIC test was done on the metal(II) complexes that showed at least 15 mm diameter of zone of inhibition. Bacteria were inoculated on nutrient agar slants and incubated for 24 h at 37°C while fungi were inoculated on potato dextrose agar slants and incubated for 72 h at 37°C. MIC tests were run with the third subculture of microbes and samples were taken during the exponential phase of the microorganisms' growth. Microbial inocula were prepared at approximately 10^5 colony forming units (CFU)/mL. The concentration of each test



Scheme 1: Synthesis Procedure for the Schiff Base.

The equations of reaction for the synthesis of metal(II) complexes can generally be written as:

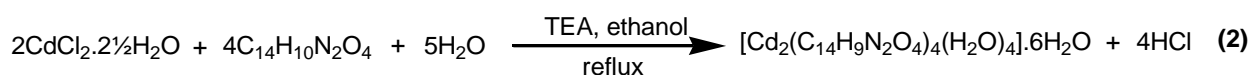
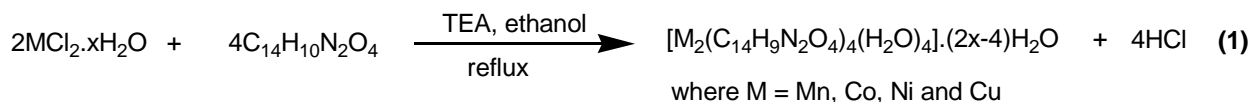


Table 1: Analytical Data of the Schiff Base Ligand (HL) and its Complexes.

Compound	Molecular Weight	Color	Melting Point (°C)	Found (Calculated) (%)				μ_{eff} / M (BM)	Yield (%)	Λ_m ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$)
				C	H	N	M			
HL $\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_4$	270.06	Yellow	209-210						70	
$[\text{Mn}_2(\text{L})_4(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O}$ $\text{C}_{56}\text{H}_{52}\text{N}_8\text{O}_{24}\text{Mn}_2$	1330.93	Off white	>360	49.66 (50.54)	3.91 (3.94)	8.03 (8.42)	8.02 (8.26)	5.6	23	7.50
$[\text{Co}_2(\text{L})_4(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O}$ $\text{C}_{56}\text{H}_{52}\text{N}_8\text{O}_{24}\text{Co}_2$	1338.92	Pale pink	>360	49.90 (50.32)	3.69 (3.91)	8.19 (8.37)	9.02 (8.80)	5.2	18	2.92
$[\text{Ni}_2(\text{L})_4(\text{H}_2\text{O})_4] \cdot 8\text{H}_2\text{O}$ $\text{C}_{56}\text{H}_{60}\text{N}_8\text{O}_{28}\text{Ni}_2$	1410.50	Green	>360	45.94 (47.69)	4.47 (4.29)	7.39 (7.94)	9.20 (8.32)	3.3	19	2.33
$[\text{Cu}_2(\text{L})_4(\text{H}_2\text{O})_4]$ $\text{C}_{56}\text{H}_{44}\text{N}_8\text{O}_{20}\text{Cu}_2$	1276.08	Green	>360	50.23 (52.71)	3.67 (3.48)	8.26 (8.78)	9.88 (9.96)	1.9	21	2.44
$[\text{Cd}_2(\text{L})_4(\text{H}_2\text{O})_4] \cdot 6\text{H}_2\text{O}$ $\text{C}_{56}\text{H}_{56}\text{N}_8\text{O}_{26}\text{Cd}_2$	1481.90	Cream	>360	44.93 (45.39)	3.33 (3.81)	7.42 (7.56)	15.82 (15.17)	0.6	42	4.14

compound in the first well was 250 $\mu\text{g/mL}$, which was serially diluted (double-fold) to the tenth well.

RESULTS AND DISCUSSION

The condensation reaction of 2-aminobenzoic acid and 3-nitrobenzaldehyde under reflux conditions was used to prepare the Schiff base ligand (HL). The ligand was subsequently reacted with chloride salts of Mn(II), Co(II), Ni(II), Cu(II) and Cd(II) to form corresponding metal complexes. The synthetic routes of the ligand and the metal(II) complexes are given in Scheme 1 and Equations (1) and (2), respectively.

The ligand and metal complexes are of different colors: the ligand is yellow while the complexes of Mn(II), Co(II), Ni(II), Cu(II) and Cd(II) are off-white, pink, light green, green and cream colors respectively. The ligand is soluble in ethanol, acetone, methanol, *N*-methylformamide, *N,N'*-dimethylformamide (DMF) and dimethylsulfoxide (DMSO) while the metal complexes are only soluble in DMSO. The Schiff base melted at 209-210°C and the metal(II) complexes have melting points above 360°C. The results of the elemental analysis (C, H, N, M) are in close agreement with the calculated values and showed the ligand coordinated to the metal ions in ratio 2:1.

FT-IR Spectra

Selected and important infrared data are presented in Table 2. Coordination of the ligand to the metal was investigated by comparing the IR bands of the ligand to those of the metal complexes. The spectrum of the free ligand showed a band at 1612 cm^{-1} characteristic of the $\nu_{\text{C=N}}$ (azomethine) stretching mode. This indicated the formation of the Schiff base as this band is absent in the spectra of the reactants. Bands of similar intensity were observed in the metal complexes in the range 1614-16219 cm^{-1} and assigned as $\nu_{\text{C=N}}$ (azomethine).

These values are quite close to those observed in the Schiff base ligand (1612 cm^{-1}) which suggests the azomethine nitrogen is not involved in complexation with the different metal(II) ions. It was reported that a shift of 15-20 cm^{-1} would suggest the coordination of azomethine nitrogen to metal ions (Chohan *et al.*, 2006). An intense band at 1710 cm^{-1} in the Schiff base is assigned as the $\nu_{\text{C=O}}$ (carboxylic group) (Abbs Fen Reji *et al.*, 2013). This band is absent in the spectra of the metal complexes.

Two characteristic strong bands observed at 1587-1592 and 1388–1409 cm^{-1} are attributed to the asymmetric $\nu_{\text{asy}}(\text{COO}^-)$ and symmetric $\nu_{\text{sym}}(\text{COO}^-)$ carboxylate stretches respectively, indicating the coordination of the carboxylate oxygen to metal ions in the complexes. This showed the carboxylic proton was abstracted in the alkaline reaction medium. The mode of coordination of the carboxylate can be deduced from the magnitude of separation between the $\nu_{\text{asy}}(\text{COO}^-)$ and $\nu_{\text{sym}}(\text{COO}^-)$, that is, $\Delta\nu(\text{COO}^-)$ (Raman *et al.*, 2009, Mautner *et al.*, 2011; Singh and Singh, 2012). For the synthesized metal complexes, values for $\Delta\nu(\text{COO}^-)$ are in the range 181-199 cm^{-1} and indicate the symmetrical bridging mode of the carboxylate (Jennifer and Muthiah, 2013). This could indicate the presence of carboxylate bridging mode of metal-oxygen-carbon-oxygen-metal (M-O-C-O-M) type between two metal centers in each complex.

New bands are observed in the spectra of the metal complexes in the far infrared regions at 467–482 cm^{-1} characteristic of $\nu(\text{M-O})$ stretching vibration, which are absent in the ligand spectra.

Table 2: IR (cm^{-1}) and UV-Visible Spectra (nm) of the Compounds.

Compound	$\nu(\text{C=N})$	$\nu(\text{C=O})$	$\nu_{\text{asy}}(\text{COO}^-)$	$\nu_{\text{sym}}(\text{COO}^-)$	$\Delta\nu(\text{COO}^-)$	$\nu(\text{H}_2\text{O})$	$\nu(\text{M-O}), \nu(\text{M-OH}_2)$	Wavelength λ_{max} (cm^{-1})
HL	1612 m	1710						25530, 28160, 36760
$[\text{Mn}_2(\text{L})_4(\text{H}_2\text{O})_4].4\text{H}_2\text{O}$	1614 m		1590 s	1409 m	181	586 b, 3462 b	474 w, 515 w	17760, 18860, 27240
$[\text{Co}_2(\text{L})_4(\text{H}_2\text{O})_4].4\text{H}_2\text{O}$	1615 m		1591 s	1408 m	183	606 b, 3478 b	467 w, 518 w	17700, 19490, 27770, 36360
$[\text{Ni}_2(\text{L})_4(\text{H}_2\text{O})_4].8\text{H}_2\text{O}$	1616 m		1592 s	1407 m	185	589 b, 3414 b	473 w, 520 w	17790, 27320, 34220
$[\text{Cu}_2(\text{L})_4(\text{H}_2\text{O})_4]$	1619 m		1587 s	1388 m	199	590 b, 3413 b	475 w, 484 w	17390, 27670
$[\text{Cd}_2(\text{L})_4(\text{H}_2\text{O})_4].6\text{H}_2\text{O}$	1616 m		1589 s	1403 m	186	611 b, 3412 b	482 w, 517 w	24270, 27890

$$\Delta\nu(\text{COO}^-) = \nu_{\text{asy}}(\text{COO}^-) - \nu_{\text{sym}}(\text{COO}^-)$$

Table 3: Diameter of Zones of Inhibition (mm) of Compounds.

Compounds	<i>B. subtilis</i> ATCC 6633	<i>S. aureus</i> ATCC 6538	<i>MRSA</i>	<i>E. coli</i> ATCC 25922	<i>E. coli</i> ATCC 23218	<i>S. typhi</i> ATCC 33458	<i>K. pneumoniae</i> ATCC 13883	<i>P. aeruginosa</i> ATCC 29853	<i>C. albicans</i> ATCC 10231	<i>Trichophyton rubrum</i> ATCC 28189
HL	12	12	12	12	12	12	12	12	12	12
DMSO	12	12	12	12	12	12	12	12	12	12
$[\text{Mn}_2(\text{L})_4(\text{H}_2\text{O})_4].4\text{H}_2\text{O}$	12	12	17	12	12	17	12	12	21	18
$[\text{Co}_2(\text{L})_4(\text{H}_2\text{O})_4].4\text{H}_2\text{O}$	12	16	19	12	12	17	12	12	16	12
$[\text{Ni}_2(\text{L})_4(\text{H}_2\text{O})_4].8\text{H}_2\text{O}$	12	12	12	12	12	12	12	12	12	12
$[\text{Cu}_2(\text{L})_4(\text{H}_2\text{O})_4]$	12	12	12	12	12	12	15	12	12	12
$[\text{Cd}_2(\text{L})_4(\text{H}_2\text{O})_4].6\text{H}_2\text{O}$	17	20	16	17	17	20	20	16	22	30
Imipenem	38	18	17	24	20	12	24	30	-	-

The complexes also exhibited additional $\nu(\text{M}-\text{O})$ band in the range $484\text{--}520\text{ cm}^{-1}$ due to coordinated water (Lima *et al.*, 1999). The broad bands in the region $3412\text{--}3478\text{ cm}^{-1}$ and $589\text{--}611\text{ cm}^{-1}$ in the spectra of all the complexes are attributed to water of crystallization (Lima *et al.*, 1999, Pradzynski *et al.*, 2012; Meshitsuka *et al.*, 1971).

Conductance Measurements

The data for conductance measurements are presented in Table 1. The molar conductances of the metal complexes in DMSO are in the range $2.33\text{--}9.50\ \Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$, showing that they are non-electrolytes and neutral complexes in DMSO solvent (Geary, 1971).

Electronic Spectra

The electronic spectra are presented in Table 1. The Schiff base ligand showed absorption bands at 25530 cm^{-1} (392 nm), 28160 cm^{-1} (355 nm) and 36760 cm^{-1} (272 nm) are assigned to $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ intra ligand transitions respectively. These bands appeared in all the synthesized complexes with a significant red shift as a result of coordination (Abbs Fen Reji *et al.*, 2013; Housecroft and Sharpe, 2005).

The electronic spectrum of Mn(II) complex consists of two bands of low intensity at 17760 cm^{-1} (563 nm), and 18860 cm^{-1} (530 nm) assigned to ${}^6A_{1g}\rightarrow{}^4T_{1g}$ and ${}^6A_{1g}\rightarrow{}^4T_{2g}$ transitions respectively for high spin octahedral geometry (Al-Shaalan, 2011). Mn(II) complex with a d^5 configuration has ${}^6A_{1g}$ ground state for high-spin octahedral system, which gives rise to 4G , 4D and 4P excited states. As there are no excited terms of sextet spin multiplicity, spin allowed $d-d$ transitions are not expected. Considering Laporte's rule, these transitions are also forbidden for octahedral complexes. So the $d-d$ transitions in a high spin octahedral Mn(II) complex are forbidden on two grounds; Laporte forbidden and spin forbidden and thus, have an extremely low molar extinction coefficient value (Housecroft and Sharpe, 2005).

The spectrum of Co(II) complex showed absorptions at 17700 cm^{-1} (565 nm) and 19490 cm^{-1} (513 nm) assigned to ${}^4T_{1g}(\text{F})\rightarrow{}^4T_{2g}(\text{F})$ and ${}^4T_{1g}(\text{F})\rightarrow{}^4T_{1g}(\text{P})$ transitions respectively, consistent with a high spin octahedral geometry

(Chohan *et al.*, 2006). The Ni(II) complex showed $d-d$ bands at 17790 cm^{-1} (562 nm) assigned to the transition ${}^3A_{2g}(\text{F})\rightarrow{}^3T_{1g}(\text{F})$ as expected for octahedral configuration (Chohan *et al.*, 2006 and Al-shaalan, 2011). The electronic spectrum of Cu(II) complex exhibited bands at 17390 cm^{-1} (584 nm) assigned to the transition ${}^2E_g\rightarrow{}^2T_{2g}$ and this is expected for an octahedral d^9 configuration (Chohan *et al.*, 2006). Cd(II) complex exhibited no $d-d$ band but showed a single band at 24270 cm^{-1} (412 nm) and is assigned to metal-ligand charge transfer (MLCT) which is indicative of octahedral geometry (Saghatforoush *et al.*, 2008).

Magnetic Susceptibility Measurements

The magnetic moments of the metal complexes were measured at room temperature and the results are recorded in Table 1. The magnetic moment of Mn(II) complex was obtained as 11.2 BM (5.6 BM per Mn(II) ion). This value is slightly less than the expected value for high spin octahedral Mn(II) ion (5.7–6.0 BM) but is consistent with the reported literature value (Mahata *et al.*, 2010).

Co(II) complex has magnetic moment of 10.4 BM (5.2 BM per Co(II) ion) which falls within the expected range (4.7–5.2 BM) of high-spin Co(II) complex. Magnetic susceptibility of 6.6 BM (3.3 BM per Ni(II) ion) was observed for Ni(II) complex. This value falls within the expected magnetic moment of paramagnetic high-spin Ni(II) ion (Al-Shaalan, 2011). The magnetic moment of 3.8 BM (1.9 BM per Cu(II) ion) was observed for Cu(II) complex. This is in agreement with the expected magnetic moment of d^9 Cu(II). The obtained values suggest paramagnetic behavior at room temperature.

The Cd(II) complex has magnetic susceptibility value of 1.2 BM (0.6 BM per Cd(II) ion), confirming its diamagnetic characteristic (Sonmez, 2001). These results are indicative of coupling interactions between two metal(II) ions in a dimeric or polymeric arrangement in the complexes. Further investigations on the temperature-dependent behavior of these metal complexes are necessary to ascertain the nature of magnetic interactions between metals.

IN-VITRO ANTIMICROBIAL SCREENING

Diameters of Zones of Inhibition

In-vitro antimicrobial activity of the compounds was determined using the diameter of zones of inhibition and the results are presented in Table 3. At the concentration tested (500 µg/well), the ligand was inactive against any of the microbial strains screened. Antimicrobial activity increased on coordination with the various metal(II) ions. Chohan and coworkers (2002, 2003 and 2004) suggested that ligands with nitrogen and oxygen donor systems might inhibit enzyme production in biological systems, since the enzymes which require these groups for their activity appear to be more susceptible to deactivation by the metal ion on complexation. They also suggested that the hydrophobic character and liposolubility of metal complexes in crossing microbial cell membranes is increased upon chelation by ligands, which reduce their polarity. Hence, their biological utilization ratio and activity of the metal complexes are greatly enhanced.

Pseudomonas aeruginosa ATCC 29853, and *Escherichia coli* ATCC 23218 showed resistance toward the complexes of Mn(II) but the complex showed activity against *Methicillin-resistant staphylococcus aureus* (MRSA), *Salmonella typhi* ATCC 33458 *Candida albicans* ATCC 10231 and *Trichophyton rubrum* ATCC 28189 with inhibitory zones between 17 and 21 mm.

Co(II) complex exhibited varying activity towards *Staphylococcus Aureus* ATCC 6538, *Methicillin-resistant staphylococcus aureus* (MRSA), *Salmonella typhi* ATCC 33458 and *Candida albicans* ATCC 10231 with inhibitory zones in the

range 16–17 mm. Ni(II) complex was not active against any of the microbial strains tested.

The complex of Cu(II) was only active against *Klebsiella pneumonia* ATCC 13883 with inhibition zone of 15 mm. Cd(II) complex showed activity against all the bacteria strains tested for with zones of inhibition range of 16–20 mm and it showed greater inhibition against pathogens such as *S. aureus*, MRSA, *S. typhi*, *E. coli* ATCC 23218 and *K. pneumonia*.

Minimum inhibitory concentration (MIC)

Table 4 shows the MIC results of the metal complexes against some selected bacteria based on the results of the *in-vitro* antibacterial screening. Using serial dilution, the concentration of the metal complexes was varied so as to determine the least concentrations of the metal complexes that are biologically active against the microbial isolates. Mn(II) complex exhibited its lowest inhibitory concentration at 31.25 µg/mL against *C. albicans* and *T. rubrum*. The Co(II) compound showed minimum inhibitory concentration at 31.25 µg/mL against *S.aureus* and *S. Typhi* and at 62.5 µg/mL against *C. albicans*. At the minimum concentration of 31.25 µg/mL, Cu(II) complex could inhibit the growth of *K. pneumonia* ATCC 13883. Cd(II) compound did not show any activity against *E. Coli* ATC 23218 at a lower concentration than 250 µg/mL. Cd(II) inhibited the growth of other microorganisms at minimum concentrations between 15.6 and 125 µg/mL.

Table 4: Minimum Inhibitory Concentration (µg/mL) of Test Compounds.

Compounds	<i>B. subtilis</i> ATCC 6633	<i>S. aureus</i> ATCC 6538	MRSA	<i>E. coli</i> ATCC 25922	<i>E. coli</i> ATCC 23218	<i>S. typhi</i> ATCC 33458	<i>K. pneumonia</i> ATCC 13883	<i>P. aeruginosa</i> ATCC 29853	<i>C. albicans</i> ATCC 10231	<i>Trichophyton rubrum</i> ATCC 28189
[Mn ₂ (L) ₄ (H ₂ O) ₄].4H ₂ O	250	250	62.5	250	250	125	250	250	31.25	31.25
[Co ₂ (L) ₄ (H ₂ O) ₄].4H ₂ O	250	31.25	250	250	250	31.25	250	250	62.5	250
[Cu ₂ (L) ₄ (H ₂ O) ₄]	250	250	250	250	250	250	31.25	250	250	250
[Cd ₂ (L) ₄ (H ₂ O) ₄].6H ₂ O	31.25	62.5	31.25	250	125	31.25	31.25	31.25	15.6	31.25

CONCLUSION

We have reported in this paper the synthesis of homodinuclear metal complexes of manganese(II), cobalt(II), nickel(II), copper(II), and cadmium(II) with a potential bidentate Schiff base ligand. The metal complexes were characterized by elemental analysis, EDTA complexometric titration, FT-IR and UV-Visible spectra, and conductance and magnetic susceptibility measurements. Each metal(II) ion in the complexes adopted a distorted octahedral geometry and the symmetrical doubly bridging carboxylate group holds the metals together.

The analytical data revealed that the ligand coordinated to the metal ions in the ratio 2:1, through the OO chromophores forming complexes of the type $[M_2L_4(H_2O)_4].xH_2O$ with distorted octahedral geometry. The OO chromophore in the carboxylate group acts as the bridge between two metal centers and forming metal-oxygen-carbon-oxygen-metal (M-O-C-O-M) bonds, which facilitate the interaction between the metal centers as suggested by the room temperature magnetic measurements. Coordination through the azomethine nitrogen was not probably observed as a result of steric hindrance by the adjacent carboxylate. The metal(II) complexes demonstrated better *in-vitro* antimicrobial activity relative to the ligand.

The following structure is proposed for the metal(II) complexes based on results from physical and spectroscopic analysis of the compounds, as shown in Figure 1.

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COMPETING INTERESTS

The authors declare that there is no conflict of interests.

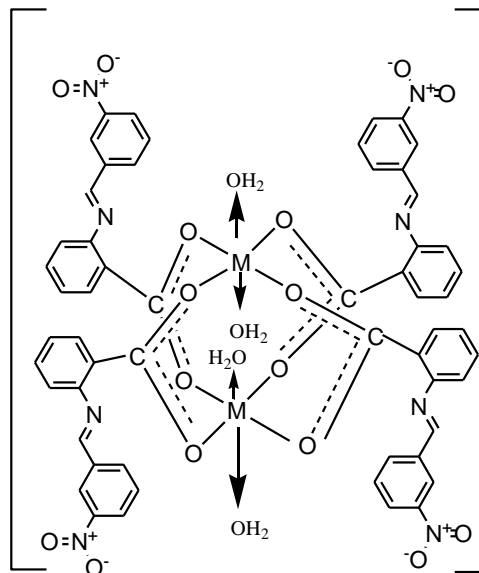


Figure 1: Proposed Structure of the Metal(II) Complexes.

REFERENCES

1. Abbs Fen Reji, T.F., A.J. Pearl, and B.A. Rosy. 2013. "Synthesis, Characterization, Cytotoxicity, DNA Cleavage and Antimicrobial Activity of Homodinuclear Lanthanide Complexes of Phenylthioacetic Acid". *Journal of Rare Earths*. 31(10):1009 – 1016.
2. Al-Shaalan, N.H. 2011. "Synthesis, Characterization and Biological Activities of Cu(II), Co(II), Mn, Fe(II), and UO₂(VI) Complexes with a New Schiff Base Hydrazone: O-hydroxyacetophenone-7-chloro-4-quinoline hydrazone". *Molecules*. 16(10):8629 – 8645.
3. Chohan Z.H., A. Scozzafava, and C.T. Supuran. 2002. "Unsymmetrical 1,1'-Disubstituted Ferrocenes: Synthesis of Co(II), Cu(II), Ni(II) and Zn(II) Chelates of Ferrocenyl -1- thiadiazolo-1'- tetrazole, -1-thiadiazolo-1'- triazole and -1- tetrazolo-1'-triazole with Antimicrobial Properties". *Journal of Enzyme Inhibition and Medicinal Chemistry*. 17(4): 261 – 266.
4. Chohan, Z.H., M. Arif, A.M. Akhtar, and C.T. Supuran. 2006. "Metal-Based Antibacterial and Antifungal Agents: Synthesis, Characterization and In Vitro Biological Evaluation of Co(II), Cu(II), Ni(II) and Zn(II) Complexes with Amino Acid-Derived Compounds". *Bioinorganic Chemistry and Applications*. Article ID83131:1-13.
5. Chohan, Z.H. 2004. "Synthesis and Biological Properties of Cu(II) Complexes with 1,1'-

- Disubstituted Ferrocenes". *Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry*. 34(5): 833 – 846.
6. Chohan, Z.H., A. Scozzafava, and C.T. Supuran. 2003. "Synthesis of Biologically Active Co(II), Ni(II) and Zn(II) complexes of Symmetrically 1,1'-Disubstituted Ferrocene-Derived Compounds". *Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry*. 33(2):241 – 257.
 7. Geary, W.J. 1971. "The Use of Conductivity Measurements in Organic Solvents for the Characterization of Coordination Compounds". *Coordination Chemistry Review*. 7:81– 122.
 8. Housecroft, C.E. and A.G. Sharpe. 2005. *Inorganic Chemistry*. 2nd Edition. Pearson Education LTD: London, UK.
 9. Jennifer S. J., and P.T. Muthiah. 2013. "Supramolecular Architectures and Structural Diversity in a Series of Lead(II) Chelates Involving 5-chloro/bromo Thiophene-2-Carboxylate and N,N'-Donor Ligands". *Chemistry Central Journal*. 7:139.
 10. Kostova, I. and L. Saso. 2013. "Advances in Research of Schiff-Base Metal Complexes as Potent Antioxidants". *Current Medicinal Chemistry*. 20 (36): 4609 – 4632.
 11. Kumar, S., D.N. Dhar, and P.N. Saxena. 2009. "Application of Metal Complexes of Schiff Bases—A review". *Journal of Scientific and Industrial Research*. 68(3): 181 – 187.
 12. Kumaran, J.S., S. Priya, N. Jayachandramani, and S. Mahalakshmi. 2013. "Synthesis, Spectroscopic Characterization and Biological Activities of Transition Metal Complexes Derived from a Tridentate Schiff Base". *Journal of Chemistry*. 2013, Article ID 260358: 10. Doi:10.1155/2013/260358.
 13. Lima, R.L.D., L.R.D.S. Teixeira, T.M.G. Carneiro, and H. Beraldo. 1999. "Nickel(II), Copper(I) and Copper(II) Complexes of Bidentate Heterocyclic Thiosemicarbazones". *Journal of Brazilian Chemical Society*. 10(3):184 – 188.
 14. Mahata, P., D. Sarma, and S. Natarajan. 2010. "Magnetic Behaviour in Metal-Organic Frameworks—Some Recent Examples". *Journal of Chemical Sciences*. 122(1):19 –35.
 15. Mautner, F.A., H.J. Albering, M. Corbella, and S.S. Massoud. 2011. "A Unique Unit Cell Containing Simultaneous Doubly and Triply Copper(II) Complexes Bridging by 2,4-Pyridine Dicarboxylate. Synthesis, Structural Characterization and Magnetic Properties". *Inorganic Chemistry Communications*. 14(5):702 – 705.
 16. Meshitsuka, S., H. Takahashi, and K. Higasi. 1971. "Infrared Spectra and Lattice Vibrations of $\text{LiSO}_4 \cdot \text{H}_2\text{O}$ ". *Bulletin of the Chemical Society of Japan*. 44:3255 – 3259.
 17. Mounika, K., B. Anupama, J. Pragathi, and C. Gyanakumari. 2010. "Synthesis, Characterization and Biological Activity of a Schiff Base Derived from 3-Ethoxy Salicylaldehyde and 2-Amino Benzoic acid and its Transition Metal Complexes". *Journal of Scientific Research*. 2(3): 513 – 524.
 18. National Committee for Clinical Laboratory Standard. 1999. Methods for Anti-Microbial Dilution and Disk Susceptibility Testing of Infrequently Isolated or Fastidious Bacteria; Approved Guideline Document M45-A 26(19). NCCLS: Villanova, PA.
 19. Pradzynski, C.C., R.M. Forck, T. Zeuch, P. Slavíček, and U. Buck. 2012. "A Fully Size-Resolved Perspective on the Crystallization of Water Clusters". *Science*. 337 (6101):1529 – 1532.
 20. Prakash, A. and D. Adhikari. 2011. "Application of Schiff Bases and their Metal Complexes-A Review". *International Journal of ChemTech Research*. 3(4):1891 – 1896.
 21. Prashanth, M.K., M. Madaiah, H.D. Revanasiddappa, and K.N. Amruthesh. 2013. "Synthesis, Characterization, and BSA Binding Studies of Some New Benzamides Related to Schiff Base". *ISRN Organic Chemistry*. Article ID 791591, 12 pg. <http://dx.doi.org/10.1155/2013/791591>.
 22. Raman, N., J. Joseph, A. Sakthivel, and R. Jeyamurugan. 2009. "Synthesis, Structural Characterization and Antimicrobial Studies of Novel Schiff Base Copper(II) Complexes". *Journal of the Chilean Chemistry Society*. 54(4):354 – 357.
 23. Saghatforoush, L.A., A. Aminkhani, S. Ershad, G. Karimnezhad, S. Ghammamy, and R. Kabiri. 2008. "Preparation of Zinc(II) and Cadmium(II) Complexes of the Tetradentate Schiff Base Ligand 2-((E)-(2-(2-(pyridine-2-yl)-ethylthio)ethylimino)methyl)-4-bromophenol (PyrBrsalH)". *Molecules*. 13(4): 804 – 811.
 24. Shit, S., J. Chakraborty, B. Samanta, G. Pilet, and S. Mitra. 2009. "A Novel Centrosymmetric Dinuclear Cadmium(II) Schiff Base Complex with Unusual Bridging Carboxylate: Synthesis, Crystal structure and Luminescence Properties". *Journal of Molecular Structure*. 919(1–3): 361 – 365.
 25. Siddiqi, Z.A., I.A. Ansari, F. Sama, and M. Shahid. 2014. "Synthesis and Characterization of a Carboxylate Bridged Homodinuclear Co(II)

complex: Crystal Structure of [Co₂(Pda)₂(H₂O)₅].2H₂O (H₂Pda = pyridine-2,6-dicarboxylic acid)". *International Journal of Innovative Research in Science, Engineering and Technology*. 3(1):8673 – 8679.

26. Singh, H.L. and J. Singh. 2012. "Synthesis, Spectral, 3D Molecular Modeling and Antibacterial Studies of Dibutyltin (IV) Schiff Base Complexes Derived from Substituted Isatin and Amino Acids". *Natural Science*. 4(3):170–178. <http://dx.doi.org/10.4236/ns.2012.43025>.
27. Sonmez, M. 2001. "Synthesis and Characterization of Copper(II), Nickel(II), Cadmium(II), Cobalt(II) and Zinc(II) Complexes with 2-Benzoyl-3-hydroxy-1-naphthylamino-3-phenyl-2-propen-1-on". *Turkish Journal of Chemistry*. 25:181 – 185.
28. Yang, G., H. Chen, Z. Zhou, and X. Chen. 1999. "Synthesis and Crystal Structures of Quadruply Carboxylate-Bridged Dimeric Lanthanide(III) Complexes of Betaine". *Journal of Chemical Crystallography*. 29(3): 309 – 316.

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